PB85-153534

Size Distributions of Elemental Carbon in Atmospheric Aerosols

California Univ., Los Angeles

Prepared for

Environmental Protection Agency
Research Triangle Park, NC

Jan 85

U.S. Department of Commerce
National Technical Information Service
NTIS

PB85-153534

EPA/600/D-85-003

SIZE DISTRIBUTIONS OF ELEMENTAL CARBON IN ATMOSPHERIC AEROSOLS

by

Antonio H. Miguel
Department of Chemistry, PUC/RJ
R.Marques de S.Vicente,225
Rio de Janeiro 22453, Brazil

Sheldon K. Friedlander
Department of Chemical Engineering
University of California, Los Angeles
Los Angeles CA 90024

EPA Grant CR810455-01

EPA Project Officer
James Cheney

ATMOSPHERIC SCIENCES RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
RESEARCH TRIANGLE PARK, NC 27711

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA/600/D-85/003	2.
3. RECIPIENT'S ACCESSION NO. PB85 153534/AS	
4. TITLE AND SUBTITLE Size Distributions of Elemental Carbon In Atmospheric Aerosols	5. REPORT DATE January 1985 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) A.H. Miguel and S.K. Friedlander	8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS University of California, Los Angeles School of Engineering and Applied Science Los Angeles, CA 90024	10. PROGRAM ELEMENT NO. CDTA1D/01 Task 2267 (FY85) 11. CONTRACT/GRANT NO. CR-810455-01
12. SPONSORING AGENCY NAME AND ADDRESS Atmospheric Sciences Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Research Triangle Park, North Carolina 27711	13. TYPE OF REPORT AND PERIOD COVERED 14. SPONSORING AGENCY CODE EPA/600/09
15. SUPPLEMENTARY NOTES	

16. ABSTRACT

Environmental problems caused by atmospheric aerosols are well documented in the specialized literature. Studies reporting on the role of dense clouds of soil particles in past mass extintions of life on Earth and, more recently (Turco et al., 1983), on calculations of potential global effects of dust and aerosol clouds (generated in a nuclear war) have received the attention of the public through oral and written reports by the news media. Because of the importance played by particulate elemental carbon (PEC) on climatic impact, a study was conducted on the size distribution of PEC in samples collected: i) in an urban area, ii) inside the air duct of an urban tunnel, and iii) next to the take-off runway of a busy airport. Besides providing needed data to improve the precision of calculations of potential local and global environmental effects, the PEC size distributions reported in this study help understand the mechanism of association of PEC and polycyclic aromatic hydrocarbons (PAHs), a class of organic compounds that include several mutagens.

17. KEY WORDS AND DOCUMENT ANALYSIS		
a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC	19. SECURITY CLASS (This Report) UNCLASSIFIED 20. SECURITY CLASS (This page) UNCLASSIFIED	21. NO. OF PAGES 8 22. PRICE

EPA Form 2220-1 (Rev. 4-77) PREVIOUS EDITION IS OBSOLETE

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

SIZE DISTRIBUTIONS OF ELEMENTAL CARBON IN ATMOSPHERIC AEROSOLS

Antonio H. Miguel[1] and Sheldon K. Friedlander[2]
[1] Department of Chemistry, PUC/RJ, R.Marques de S.Vicente,225
Rio de Janeiro 22453, Brazil
[2] Department of Chemical Engineering, UCLA, CA, 90024, USA

Introduction

Environmental problems caused by atmospheric aerosols are well documented in the specialized literature. Studies reporting on the role of dense clouds of soil particles in past mass extinctions of life on Earth and, more recently (Turco et al.,1983), on calculations of potential global effects of dust and aerosol clouds (generated in a nuclear war) have received the attention of the public through oral and written reports by the news media. Because of the importance played by particulate elemental carbon (PEC) on climatic impact, a study was conducted on the size distribution of PEC in samples collected: i) in an urban area, ii) inside the air duct of an urban tunnel, and iii) next to the take-off runway of a busy airport. Besides providing needed data to improve the precision of calculations of potential local and global environmental effects, the PEC size distributions reported in this study help understand the mechanism of association of PEC and polycyclic aromatic hydrocarbons (PAHs), a class of organic compounds that include several mutagens.

EXPERIMENTAL

Sampling

The urban area sample was collected on the roof (7th floor) of Boelter Hall on the UCLA Campus. Sampling was carried out for a 24-hour period in the summer. Averaged-fleet aerosol emissions were sampled inside the air duct of the Caldecott Tunnel, on a freeway commuter route east of Berkeley. The tunnel is 1.1 Km long, carrying two lanes of uphill traffic with a 2 degree grade. Sampling was conducted in the summer for a period of 226 minutes. Aircraft-dominated aerosols were collected about 50 meters from the take-off area of large aircrafts on Runway 26 of Los Angeles International Airport (LAX). Sampling time was 336 minutes. All samples were collected using a calibrated eight-stage low-pressure impactor (LPI) with 50% efficiency cut-offs of 4.0, 2.0, 1.0, 0.5, 0.26, 0.12, 0.075, and 0.050 µm aerodynamic diameter, dp (Hering et al., 1978,1979). During sampling at both the airport and in the tunnel, a cyclone (Johns and Wall, 1981) was connected to the inlet of the LPI to remove particles resulting from resuspension which could overload the impaction discs of the LPI. Particle bounce in the LPI was reduced by a layer of Vaseline about 2 µm thick by about 3 mm diameter (Miguel, 1982) deposited on unbaked pre-cleaned stainless steel (ss) strips mounted onto 2.54 cm diameter glass discs.

Instrumentation and Analytical Procedure

All PEC determinations were made using a Dohrmann Carbon Analyser (DCA) model DC-50A/52A operated in the total carbon mode and manual boat injection. The DCA's original sample port was modified to allow passage of the ss strips. Manganse dioxide powder was used as oxidant in the PEC determination of the ambient air sample. For the other two samples, only zero air was used to oxidize PEC. The first step in the analysis procedure was to vaporize the Vaseline and all non-elemental carbon compounds (low boilers) contained in the sample. This was done under anaerobic (Helium) conditions by sliding the Pt boat containing the ss strips onto the vaporization zone , operated at 120±10 degrees C for a period of 148 seconds and then onto the pyrolysis zone operated at 530±15 degrees C for a period of 298 seconds. Vaseline blanks were carried out in the same manner. The temperature in the pyrolysis zone was then raised to 825±20 degree C and allowed to stabilize for about 2 hours. At this point zero air was introduced into the sample port at a rate of 18 cc/min. Potassium acid phathalate (KHP) standards were run to set the appropriate instrument span. Activated carbon (Aldrich 24,227-6, Darco 6-60, 100-250 mesh) suspensions preparared in water (using an ultrasonic device) deposited on ss strips were used to validate the method. Further details of the analytical procedure employed can be found elsewhere (Miguel, 1984).

At 825 degrees C, under aerobic conditions, PEC is oxidized to carbon dioxide which is then reduced to methane by a bed of nickel catalyst. The methane formed is quantitated by the flame ionization detector of the DCA. The digital readings of the detector (ppm) are converted to mass and the PEC mass distribution functions calculated in the usual manner. The measured PEC corresponds to the portion of the sample that is oxidized by manganese dioxide or air.

RESULTS AND DISCUSSION

The major fraction of "sooty" aerosols is comprised of a mixture of elemental carbon (designated here as PEC), tars and oils (Turco et al., 1983). Among the minor constituents, perhaps the most important from a toxicological point of view are the PAHs and their -nitro and -methyl derivatives. In the ambient sample (Fig.1c), observations of the deposit on the first stage ($dp>4\mu m$) using an optical microscope revealed the presence of large quantities (perhaps larger than that of particles) of transparent, oily droplets. Upon pyrolysis, this deposit became black, indicating that the oily material was partly converted to elemental carbon, which resulted in an artificial reading of PEC concentration. For this reason, data obtained from the first stage were discarded. Since the airport and tunnel samples were collected with a cyclone connected to the LPI inlet, first stage data for these samples were also discarded.

Data on the concentration of PEC as a function of particle

size are presented in Figures 1a, 1b, and 1c, respectively for the tunnel, the airport, and the ambient air samples. In all samples, most of the PEC was found in aerosols with aerodynamic diameter below 1.0 μm. For the tunnel and airport samples, the mass of PEC associated with aerosols of aerodynamic diameter less than 0.5μm was 87 and 77%, respectively. For the ambient air sample it was 65%. These values agree qualitatively with the expected relative "age" of the aerosols in the three collection sites, that is, the tunnel aerosols should be less aged than the others. The ambient air aerosols should be aged more that the airport aerosols, since the latter are closest to an important source of PEC (aircraft exhaust) and thus had less time to coagulate and agglomerate.

While the distribution of PEC with respect to particle size was unimodal (centered between 0.05 and 1.0 μm) in the tunnel sample (Fig. 1a) it was bimodal in both the airport and the ambient air samples (Figs. 1b and 1c). The additional PEC mode in the size range between 0.5 and 1.0 μm, may have resulted from coagulation of fine PEC onto nitrates, sulfates and chlorides which, in mixed polluted/maritime air masses, have a major mode in this size range (Harrison and Pio, 1983). PEC in this size range are responsible for significant attenuation of the solar flux with attended lowering of ambient temperatures and decreased visibility. In addition, due to their large surface to volume (or mass) ratio, submicron PEC may catalyse specific chemical reactions with entrained gases near the combustion process.

The mass distribution of PEC as a function of particle size for the ambient air sample (Fig. 1c) was similar in form to typical distributions of benzo(a)pyrene (BaP) with respect to particle size (Fig.1d) in Rio de Janeiro aerosols (Miguel, 1982). This observation is consistent with an adsorption mechanism for the PAH-elemental carbon association.

Acknowledgements

The authors thank Susanne V. Hering for collecting the tunnel sample and for her invaluable help in the collection of the others. The ready cooperation of James M. Kelly, supervisor of facilities, maintenance and technical services of TWA at LAX is greatly appreciated.

This research has been funded in part by the National Research Council of Brazil (CNPq), FINEP(Brazil), and the U. S. Environmental Protection Agency under Grant CR-810455-01, and does not necessarily reflect the view of the agency and no official endorsement should be inferred.

References

Harrison, R.M, and Pio, C.A. (1983) "Size Differentiated Composition of Inorganic Atmospheric Aerosols of Both Marine and Polluted Continental Origin", Atmos.Environ. 17,1733.

Hering, S. V., Flagan, R. C., and Friedlander, S. K. (1978)

"Design and Evaluation of a New Low-Pressure Impactor I". Environ. Sci. Technol. 13: 667.

Hering, S. V., Friedlander, S. K., Richards, L. W., and Collins, J. J. (1979) "Design and Evaluation of a New Low-Pressure Impactor II." Environ. Sci. Technol. 13,184.

Johns, W., and Wall, S. (1981)"Size Selective Sampler for Particulate Monitoring in California". Air Industrial Hygene Lab., California State Dept. Health Services, Technical Report No. CA/DOH/AIHL/SP-24, October.

Miguel, A. H. (1982)"On the Determination of Benzo(a)Pyrene in Atmospheric Aerosols Fractionated by a Low Pressure Impactor, by TLC Separation and in situ Spectrophotofluorometry at the Picogram Level". Intern. J. Environ. Anal. Chem. ,12,17.

Miguel, A. H. (1984) in preparation.

Turco, R. P., Toon, O. B., Ackerman, T.P., Pollack, J. B., and Sagan, C. (1983)"Nuclear Winter: Global Consequences of Multiple Nuclear Explosions". Science ,222,1283.

Wolff, G. T., Groblicki, P. J., Cadle, S. H., and Countess, R. J. (1982)"Particulate Carbon at Various Locations in the United States". Particulate Carbon: Atmospheric Life Cycle ,(Edited by G. T. Wolff and R. L. Klimisch), Plenum Press, New York.

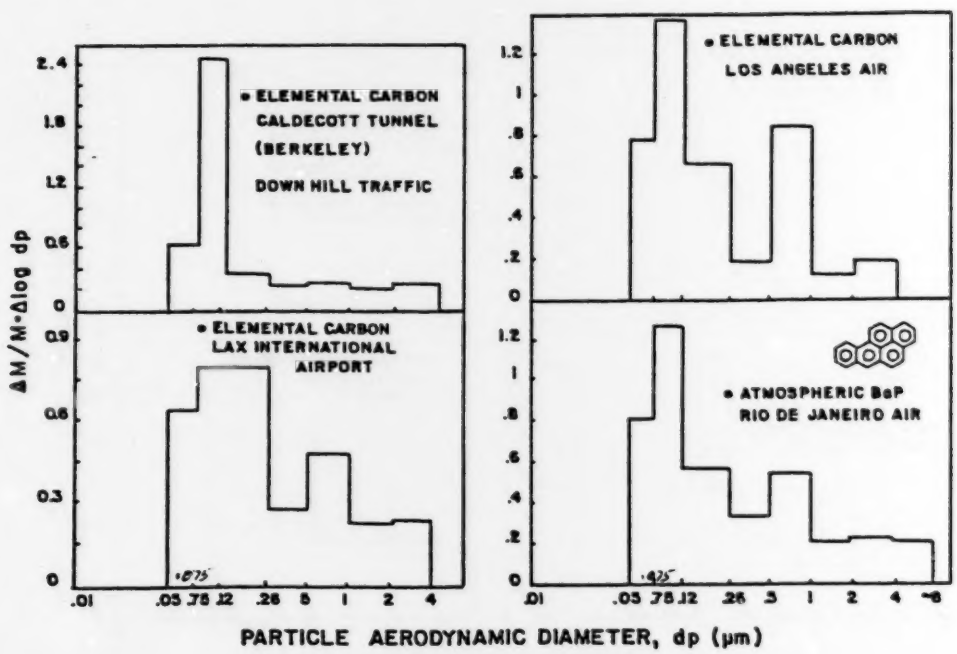

Figure 1. Mass distributions of PEC and benzo(a)pyrene as a function of particle size. PEC loadings, ΔM, ($\mu g/m^3$): 34.3, 14.4, and 2.13, respectively for 1a, 1b, and 1c. BaP loading, $\Delta M = 1.62$ ng/m^3.